Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Engineering 44 (2012) 103 – 105

Procedia Engineering

www.elsevier.com/locate/procedia

Euromembrane Conference 2012

[OA31]

Characterization of the gas transport in mixed matrix membranes based on polymers with intrinsic microporosity (PIMs)

J.C. Jansen[1], P. Bernardo*[1], F. Bazzarelli[1], G. Clarizia[1], P.M. Budd[2], Y. Yampolskii[3] et al

[1]CNR, Italy, [2]University of Manchester, UK, [3]A.V. Topchiev Institute of Petrochemical Synthesis, Russia

One of the challenges in the field of membrane science is to develop new materials with the proper combination of permeability and sufficiently high selectivity. For large volume applications such as natural gas treatment or CO_2 sequestration from flue gas, polymers with a very high permeability in combination for an acceptable selectivity are required. A limitation of pure polymeric materials is that there is generally a trade-off between the permeability and the selectivity of the membrane and in a double logarithmic plot of selectivity versus permeability the maximum performance is limited by the so-called Robeson upper bound [1]. One of the polymers which currently performs on the this upper bound for a number of interesting gas pairs is the polymer with intrinsic microporosity PIM-1 [2] (Figure 1).

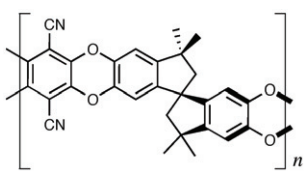

Figure 1. Structure of PIM-1 [2]

Mixed matrix membranes (MMMs) based on open porous nanofillers, dispersed in a dense polymer matrix, have the potential to overcome this upper bound by the synergistic action of the highly permeable porous filler and the selective dense polymeric matrix.

The concept of the European project *DoubleNanoMem* is to embed porous nanofillers of different kind in polymers with an already high free volume and consequently high permeability, such as PIM-1. The aim of this project is to overcome the Robeson upper bound in a region where permeability is already high.

In this work we present the gas permeation properties of PIM-1 based membranes with various metalorganic framework structures, dispersed in the polymer matrix. Three examples of structures used are given in Fig. 2. The transport properties of the PIM-1 based MMMs containing the given nanofillers will be discussed in detail. The three fundamental transport parameters (permeability, diffusivity and - indirectly - solubility), determined by gas permeability measurements, using a fixed volume pressure increase setup in the time lag mode will give insight into structure property relationships of porous fillers in high free volume polymers.

doi:10.1016/j.proeng.2012.08.324

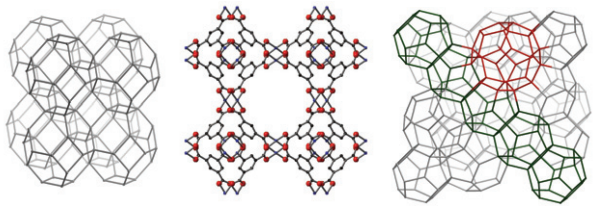

Figure 2. Illustration of the framework structures of ZIF-8 (left), HKUST-1 (middle) and MIL-101 (right).

It was found that in particular nanoZIF-8 and MIL-101 significantly enhance the performance of the MMM compared to the neat PIM-1, reaching values for CO_2/N_2 separation well above the Robeson upper bound (Figure 3).

The discussion of the results will further focus on the difference between pure gas and mixed gas permeation, on the difference between a fixed volume pressure increase setup and a constant pressure variable volume setup with mass spectrometric analysis, on the effect of feed pressure and other experimental variables.

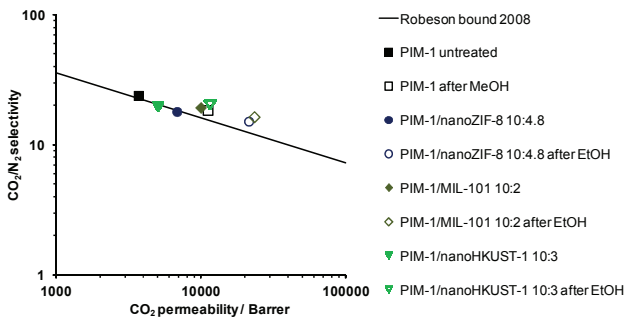

Figure 3. Robeson diagram for the CO_2/N_2 pair for neat PIM-1 and representative PIM-1 MMMs, containing the nanofillers shown in Fig. 2. Solid symbols represent the as prepared membrane and open symbols represent the ethanol-treated membranes. The solid line is Robeson's 2008 upper bound [1].

Acknowledgements

We are grateful to support from the Engineering and Physical Sciences Research Council (EPSRC) for AFB (Doctoral Training Account) and LMA (Materials World Network grant EP/G065144/1). The work leading to these results has further received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° NMP3-SL-2009-228631, project DoubleNanoMem.

References

1. Robeson, L.M., The Upper Bound revisited, *J. Membr. Sci.*, **2008**, *320*, 390.

2. P.M. Budd, N.B. McKeown, B.S. Ghanem, K.J. Msayib, D. Fritsch, L. Starannikova, N. Belov, O. Sanfirova, Y.P. Yampol'skii, V. Shantarovich, , *J. Membr. Sci*. **2008**, *235*, 851-860.

Keywords: Polymer of Intrinsic Microporosity, Solution-diffusion mechanism, mixed matrix membrane, metalorganic framework